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THEORY OF ELECTRON RECOMBINATION
IN SEMICONDUCTORS *

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We examine the recombination of conductivity electrons on charged and neutral centers. We quantitatively examine the case when the localization probability of the electron nearing the center is sufficiently high and consequently the speed of recombination is limited and is determined by the electron diffusion speed towards the recombination centers. We calculate the recombination coefficient, the average electron displacement in the external field and the electroconductivity provoked by the irradiation of the crystal with light, X-rays, α -rays or charged particles.

If the semiconductor is in a state of thermal equilibrium, then the average number of electrons on the various energy levels is easily calculated with the help of equilibrium statistics. For the calculation it is enough to know the energies and multiples of the various quantum electron conditions. It is not necessary to know the mechanism or the probability of the electron passing from one condition to the other.

It is much more difficult to examine the cases when the thermal equilibrium is upset. For instance, when an additional conductivity is created in the semiconductor by means of its irradiation with light, X-rays, α -rays or charged particles. In these cases we must use the kinetic equations and we must therefore know the electron recombination probabilities. The theoretical

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examination of the recombination with a change of energy into heat offers particular difficulties, since up to this day the mechanism of thermal recombination is not clear even in its qualitative aspect. In the kinetic equations the recombination member is usually written as: βNn , where n is the conductivity electron concentration; N is the recombination centers concentration; and β is the recombination coefficient which, usually, is defined only when theory and experiment are compared. In this work β is theoretically calculated for certain important individual cases.

RECOMBINATION COEFFICIENT

Let us suppose that the conductivity electrons find themselves in the polaronic state (1--4) and that their concentration in the semiconductor is n , while the concentration of the recombination centers is N . We assume that the latter are immobile (crystal defects) or, at least, less mobile than the polarons (holes for instance, if they have a large effective mass). If the recombination centers are positively charged, then they attract the polarons by means of their coulomb field, while if they are neutral they are dielectrically polarized by the field of the approaching polaron. As a result, a reciprocity force also arises between the polaron and the center. In a general case let us assume that the reciprocity force is described by the potential $V(r)$ and extends to a considerable distance of the order of several free polaron runs.

Let us surround the recombination centers with imaginary spherical surfaces with a small radius r and let us calculate the polaron flow inside these spheres. Thereby we assume that r

is considerably smaller than the average distance between the centers and that upon examining the flow through the given sphere we may ignore the force influence of the neighboring centers. On the other hand we assume that r is bigger than the polaron free path ~~then~~ so that in the calculation of the flow we may avail ourselves of the common electroconductivity and diffusion equations. The number of polarons entering the above-mentioned spheres in one second within the volume unit of the semiconductor is equal to

$$z = S n u \frac{dV}{dr} + S D \frac{dn}{dr}, \quad (1)$$

where u is the mobility of the polarons; D is their diffusion coefficient; and S the sum surface of all the spheres in the volume unit:

$$S = 4 \pi r^2 D, \quad (2)$$

$n(r)$ is the concentration near the multi-bonded surface consisting of the above-mentioned spheres.

These sphere encompass only an insignificant part of the whole crystal volume. Therefore the electrons excited into the conductivity zone as a result of the irradiation of the crystal will more often than not find themselves outside of these spheres after their retardment and transition into the polaronic state and therefore for the recombination they will have to pass through the spheres in the shape of a flow (1). The later very swiftly acquires a quasi-stationary character since the relaxation time is of the order of 10^{-12} seconds and less. Inasmuch as during such a brief time the number of conductivity electrons in the crystal cannot change appreciably, we may say that z is the quasi-stationary

$[10^{-12}]$

flow, not related to r ; and we may identify z with the number of recombinations taking place during one second in one volume unit.

If, from the differential equation (1) we determine $n(r)$, and say that the polaron concentration far from the recombination centers is equal to $n(\infty) = n_\infty$, and if we take into consideration the known ratio

$$D/\chi = kT/e, \quad (3)$$

then we obtain

$$n(r) = \left[n_\infty - \frac{z}{4\pi ND} \int_0^r e^{eV/kT} dx \right] \cdot e^{-eV/kT}; \quad \chi = \frac{1}{F} \cdot (4)$$

When the polaron ^{order of a} approaches the recombination center to a distance r_0 of the polaron radius ~~order~~, then there appears a certain probability of electron passage to a combined state. It is extremely difficult to calculate this probability even if the nature of the recombination center is precisely known. However we may affirm that the number of electrons passing into a combined state during one second and in one unit of volume (number of recombinations) is proportion to the number of centers N and to the concentration $n(r_0)$ of polarons in the direct vicinity of the centers. Thus the number of recombinations may be recorded as $\beta_1 N n(r_0)$, where β_1 is the unknown coefficient of proportionality. Accordingly to the formula (4)

$$n(r_0) = \left(n_\infty - \frac{z}{4\pi ND} \int_0^{r_0} e^{eV/kT} dx \right) e^{-eV(r_0)/kT}. \quad (5)$$

As we have already mentioned, in the quasi-stationary case the flow z should be equalled to the number of recombinations

$$z = \beta, N_n(r_0). \quad (6)$$

From equations (5) and (6) it follows:

$$z = \frac{\beta, N_{n\infty} e^{-eV(r_0)/kT}}{1 + \frac{\beta,}{4\pi D} e^{-eV(r_0)/kT} \int_0^{r_0} e^{eV/kT} dx} \quad (7)$$

Two cases are possible:

(A) In the denominator of formula (7) the second member

$\ll 1$. Then

$$z = \beta N_{n\infty}, \beta = \beta, e^{-eV(r_0)/kT}, \quad (8)$$

This formula does not give us anything new since the value of β is still unknown.

(B) In the denominator of formula (7) the second $\gg 1$.

In this case

$$z = \beta N_{n\infty}, \beta = 4\pi D / \int_0^{r_0} e^{eV/kT} dx \quad (9)$$

This formula offers considerable interest. It gives the possibility to calculate the recombination coefficient in various concrete cases. If the condition of case (B) is not fulfilled, then formula (9) expresses the upper limit of the recombination coefficient.

Cases (A) and (B) may be interpreted in the following fashion: in the case (A) not the attraction of the polarons to the recombination centers, but the passage of the electrons into a combined state is the "narrow spot" of the recombination process which determines its speed. Therefore the recombination coefficient β is not related to the diffusion coefficient D , (or

to the coefficient of mobility u), but is determined by the probability of the passage of the electron into a combined state (β_1). In the case (B) on the contrary, not the passage of the electron into a combined state but the attraction of the polarons to the recombination centers is the "narrow spot" determining the speed of recombination. Therefore β is not related to β_1 , but rather to D (or u). Below we speak only of the case (B).

RECOMBINATION ON POSITIVELY CHARGED CENTERS

The coefficient of reciprocity between the polarons and the center has a coulomb aspect:

$$V = -e/\epsilon r = -ex/\epsilon \quad [x = \frac{1}{r}] \quad (10)$$

where ϵ is the dielectric constant. In formula (9) one may substitute the integral from 0 to ∞ for the integral from 0 to $1/r_0$, inasmuch as usually

$$e^{-e^2/\epsilon r_0 kT} \ll 1. \quad (11)$$

Thus

$$\int_0^{1/r_0} e^{ex/\epsilon kT} dx \approx \int_0^\infty e^{ex/\epsilon kT} dx = \frac{\epsilon kT}{e^2} \quad (12)$$

Introducing this into formula (9), we get

$$\beta = 4\pi D e^2 / \epsilon kT = 4\pi e u / \epsilon, \quad (13)$$

where u is the mobility of the polarons. With such a recombination coefficient for the average time of the life of the electron in its free state we get the expression

$$t = 1/\beta N = \epsilon / 4\pi e u N. \quad (14)$$

The average electron displacement Δ under the influence of the external electrical field \mathcal{E} is obtained by multiplying it by the speed of the polaron "drift": $v = uE$,

$$\Delta = \tau u E = \varepsilon E / 4 \pi e N. \quad (15)$$

In the particular case under discussion the displacement is not related to mobility and temperature.

If the irradiation of the crystal during one second and in one volume unit excites L electrons into the conductivity zone, then in the stationary case

$$L = \beta N n_{\infty} \quad (16)$$

From here, with the help of formula (13) we get

$$\sigma = e u n_{\infty} = \varepsilon L / 4 \pi N. \quad (17)$$

is the specific electroconductivity of the crystal provoked by the stationary irradiation. Formula (17) shows that σ is not related to mobility.

RECOMBINATION ON NEUTRAL CENTERS

A neutral center is dielectrically polarized by the field of the approaching polaron^y. The dipole moment which thereby arises is equal to

$$p = \gamma e / \varepsilon r^2, \quad (18)$$

where γ is the center polarization coefficient and r is the distance from the polaron to the center. This dipole attracts the polaron^y by the field

$$E = -2p / \varepsilon r^3 = -2\gamma e / \varepsilon^2 r^5.$$

To such a field correspond the potential

$$V = -\gamma e / 2 \varepsilon^2 r^4 = -a x^4, \quad a = \gamma e / 2 \varepsilon^2 \quad (19)$$

If

$$ea/r_0^4 kT > 1 \quad (20)$$

then in formula (9) we may substitute the integral from 0 to ∞ for the integral from 0 to $1/r$. In this case

$$\int_0^{1/r_0} e^{ev/kT} dx \approx \int_0^{\infty} e^{-eax^4/kT} dx = 0.9064 (kT/ea)^{1/4}$$

Introducing this expression into formula (9), we get

$$\beta = 1.1 \frac{4\pi D}{(kT/ae)^{1/4}} = 1.1 \cdot 4\pi u \left(\frac{e^3}{a^3 (kT)^3} \right)^{1/4} \quad (22)$$

The average time of life of the electron in its free state is

$$t = \frac{1}{\beta N} = \frac{0.9064}{4\pi u N} \left(\frac{e^3}{a^3 (kT)^3} \right)^{1/4} \quad (23)$$

The average electron displacement is

$$\Delta = t u E = \frac{0.9064 E}{4\pi N} \left(\frac{e^3}{a^3 (kT)^3} \right)^{1/4} \quad (24)$$

Upon stationary irradiation of the semiconductor there appears an electroconductivity equal to

$$\sigma = \frac{0.9064 \cdot L}{4\pi N} \left(\frac{e^7}{a^3 (kT)^3} \right)^{1/4} \quad (25)$$

The application of the theory to actual crystals and the comparison of theory and experiment are given in the following article.

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